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Facile and durable antimicrobial finishing of cotton textiles using a silver salt and UV light

Marek Kozicki[a,b,*], Elżbieta Sąsiadek[a,b], Marek Kołodziejczyk[c], Justyna Komasa[d], Agnieszka Adamus[d], Waldemar Maniukiewicz[e], Aleksandra Pawlaczyk[e], Małgorzata Szynkowska[e], Jacek Rogowski[e], Edward Rybicki[a,b]

[a] Department of Man-Made Fibres, Faculty of Material Technologies and Textile Design, Lodz University of Technology, Żeromskiego 116, 90-924 Łódź, Poland
[b] European Centre of Bio- and Nanotechnology (ECBNT), Lodz University of Technology, Łódź, Poland
[c] Institute of Technical Biochemistry, Faculty of Biotechnology and Food Sciences, Lodz University of Technology, Stefanowskiego 4/10, 90-924 Łódź, Poland
[d] Institute of Applied Radiation Chemistry, Faculty of Chemistry, Lodz University of Technology, Wróblewskiego 15, 93-590 Łódź, Poland
[e] Institute of General and Ecological Chemistry, Faculty of Chemistry, Lodz University of Technology, Żeromskiego 116, 90-924 Łódź, Poland

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ABSTRACT

In this study, we present facile antimicrobial finishing of cotton textiles. Screen printing was used for surface-finishing of cotton using a printing paste containing silver nitrate. UVC irradiation was applied to convert silver nitrate into a color product, thus also changing the color of the textiles. The color, its strength and stability of samples, depend on absorbed UVC energy and the formula of the printing paste. Scanning electron microscopy with the energy dispersive X-ray spectrometry revealed formation of silver particles on cotton threads; X-ray diffraction analysis and the time-of-flight secondary ion mass spectrometry did not provide clear information on these products. Microbiological studies revealed that the samples inhibited proliferation of *Escherichia coli*, *Bacillus subtilis* and *Staphylococcus aureus*. Washing fastness tests confirmed resistance of the samples to at least 50 washings. Additionally, the inhibition zones increased as the number of washing cycles increased, which is unique for such samples. This work also presents an approach to the design of antimicrobially finished workwear.

1. Introduction

Noble metal particles are very attractive to different fields of research due to the broad range of their applications in optics, electronics, biotechnology and medicine (Atiyeh, Costagliola, Hayek, & Dibo, 2007; Choi, Lee, Jeong, Choi, & Lee, 2009; Klasen, 2000a, 2000b; Yang & Wang, 2007). The activity of silver in the form of nanoparticles or ions leads to the destruction of many Gram-positive and Gram-negative bacteria and fungi, confirming it as one of the most powerful antimicrobial agents.

Silver nanoparticles were shown to affect cell walls of *Escherichia coli* by forming pits. Some silver particles accumulated in the walls whereas others penetrated into the cells (Sondi & Salope-Sondi, 2004). Silver can affect respiratory enzymes and other structures crucial for proper functioning of a cell (Atiyeh et al., 2007). Studies have also suggested that silver nanoparticles may produce free radicals, attacking bacterial structures (Kim et al., 2007). Despite the above-mentioned beneficial effects, one should not underestimate the *in vitro* cytotoxicity of silver for human macrophage and epithelial lung cells (Soto, Garza, & Murr, 2007) or fibroblasts and keratinocytes (Poon & Burd, 2004). Bacterial resistance to silver is also reported (Atiyeh et al., 2007; Percival, Bowler, & Russell, 2005). Additionally, some adverse effects of silver stemming from accumulation in the human body after entering through different portals (for instance: local and generalized argyria, accumulation of silver in some organs) have been reported (Chen & Schluesener, 2008; Drake & Hazelwood, 2005). Contrary to these findings, a study by Bosetti, Massè, Tobin, and Cannas (2002) evidenced no cytotoxic and genotoxic effects of silver deposited on orthopedic external fixation pins, even though a release of silver from the pins was observed.

Metal nanoparticles, nanosilver included, are very often applied on textiles. A range of textiles was silver finished; however, the most often used was cotton. For instance, an environmentally friendly method of silver particles production on cotton fibers was proposed. The samples possessed some resistance to washing and antimicrobial properties (Ravindra, Mohan, Reddy, & Raju, 2010;

* Corresponding author at: Department of Man-Made Fibres, Faculty of Material Technologies and Textile Design, Lodz University of Technology, Żeromskiego 116, 90-924 Łódź, Poland.
E-mail addresses: mkozicki@mitr.p.lodz.pl, marek.kozicki@p.lodz.pl (M. Kozicki).

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Sathishkumar, Sneha, & Yun, 2010). Another group showed that silver chelation through glycidyl methacrylate-iminodiacetic acid grafting following exposition to UV light resulted in silver nanoparticles on cotton fibers exhibiting antimicrobial activity against *E. coli* (Chen & Chiang, 2008). Preparation of cotton through the chelation of silver, however, with the aid of chitosan, was also proposed elsewhere (Thomas, Bajpai, & Bajpai, 2011).

Different reducers of silver ions were used for the preparation of nanosilver functionalized cotton fabrics, for instance: sodium borohydrate in argon saturated aqueous solution – proliferation inhibition of *E. coli*, *Staphylococcus aureus* and *Candida albicans* (Ilić et al., 2009); sodium borohydrate reaction with silver cations entrapped by poly(acrylamide-co-itaconic acid) – inhibited proliferation of *E. coli* (Gupta, Bajpai, & Bajpai, 2008); ascorbic acid reaction with silver cations on alkaline cotton and hydrophobization with octyltriethoxysilane – antimicrobial action against *E. coli* and *S. aureus* (Khalil-Abad & Yazdanshenas, 2010); ascorbic acid – bacteriostatic activity against *E. coli* and *Bacillus subtilis* (Matyjas-Zgondek, Bacciarelli, Rybicki, Szynkowska, & Kołodziejczyk, 2008); ascorbic or tannic acid in the presence of polyethylene glycol (Su, Wei, Hu, & Tang, 2011): in this case the fabric had antibacterial properties against *E. coli* and *S. aureus* even after 50 washings.

Other interesting methods of cotton functionalization with silver include the sol–gel ones, those employing β-cyclodextrins or digital printing. An example for the first one is presented elsewhere (Xing, Yang, & Dai, 2007). According to the method, silver oxides on cotton were produced which resulted in an antimicrobial activity of the textile against *E. coli* even after fifty washes. An example for the second one is grafting β-cyclodextrins with acrylic acid and loading with silver nanoparticles (Hebeish, El-Shafei, Sharaf, & Zaghloul, 2011). The cotton fabric padded with such the solution withstood ten washing cycles, showing antibacterial action against *E. coli* and *S. aureus*. The digital printing as a novel method of cotton functionalization was presented elsewhere (Rybicki et al., 2010). The nanosilver was formed *in situ* on cotton that had a high resistance to washings (up to 50). This last example of silver-finished fabric certainly does not exhaust the subject of the nanosilver antimicrobial functionalization of textiles.

Despite the range of the above-given examples, only a few showed resistance of silver-finished cotton to the washing process. In this work, we present another method of *in situ* functional finishing of cotton fabric with silver products. Screen-printing of cotton with a printing paste containing silver ions was used; however, UVC was used as a developing medium of functionality directly on the surface of the textile. This work evidenced that the silver-finished cotton obtained with the proposed method is highly resistant to at least 50 washings and revealed enhanced antimicrobial activity after multiple washings: this is unique for such samples.

2. Experimental

2.1. Preparation of printing paste

In order to prepare a printing paste, a crosslinker of Helizarin Binder (aqueous nonionic dispersion, with some anionic character, of a thermally crosslinkable acrylate copolymer), a synthetic thickening agent of Lutexal HIT (acrylate-based polymer) (both BASF, Germany; distributed by BASTEX, Poland) and silver nitrate (POCh, Poland) were used. For the preparation of 200 g paste, Helizarin Binder (30 g) and Lutexal HIT (10 g) were mixed with 80 g of distilled water at 1000 rpm for 20 min. Next, 80 g of silver nitrate solution was prepared and added to the mixture of Helizarin Binder and Lutexal HIT, by continuous mixing at 1000 rpm, so that the final concentration of silver nitrate in the paste was 0.01; 0.1 and 1% (w/w). After 15 min of mixing, the paste was considered to be ready, since no further change in viscosity was observed organoleptically and the paste was homogeneous. However, to facilitate the preparation of a paste (200 g) containing 10% (w/w) silver nitrate, an altered procedure was applied. First, 20 g of silver nitrate was dissolved in 50 g of distilled water. Next, other ingredients were added using continuous mixing (1000 rpm; 30 min) in the following order: Lutexal HIT (40 g); distilled water (20 g); Helizarin Binder (30 g); Lutexal HIT (30 g); and distilled water (10 g). The paste was prepared at ~23 °C and was used for surface finishing of cotton samples immediately after preparation. The pH of the paste was not adjusted and was equal to 8–8.5.

2.2. Screen printing of samples

We used a cotton fabric (mercerized, sanforized, bleached) of a twill (3/1)*S* weave and a surface mass of 250 g/m^2, thickness 0.68 mm, weft sett 220 per dm and warp sett 240 per dm (Ten Cate, The Netherlands). The printing process was performed with the aid of a screen-printing method, as it allows uniform coverage of the surface of the cotton textile. The aqueous printing paste, which was made as described in Section 2.1, was used for printing. Before printing, however, a stencil (EX 63-063/160 PW screen: 63 mesh/cm; thread diameter 63 μm; color of mesh: white; tension: 18 N/cm; NBC, Japan; distributed by K+L Company, Poland) was prepared with a 200 mm × 300 mm rectangular pattern, through which the printing paste was transferred onto the cotton textile. This resulted in deposition of the printing paste containing silver nitrate on the cotton textile in the form of the 200 mm × 300 mm rectangle. Afterwards, printed cotton was dried in a drier (E. Benz, Switzerland) at 40 °C for 40 min. No curing at elevated temperature (over 100 °C) was applied to the samples. The pick-up of the paste by a 1 g cotton sample was equal to 0.409 g (rough estimation; no special conditioning of samples was applied). In Section 2.6.4 an approach to precise determination of silver deposition on the samples is presented.

2.3. UV irradiation

Surface-finished cotton samples with a paste containing silver nitrate were irradiated with a UV-curing cabinet to deliver doses of up to 10 J/cm^2 (an instrument of UVP, UK, equipped with a lamp Type G8T5, 8 W with UV output of 2.5 W, 253.7 nm, Sankyo Denki, Japan). For this instrument the energy of J/cm^2 had to be specified before irradiation, and was afterwards emitted automatically. The time required to emit, *e.g.*, 500 [mJ/cm^2] was equal to 102 s.

With the aid of UVC meter (254 nm; LTLutron, CYFRONIKA S.C., Poland), we found that the cotton samples used in this experiment absorbed 98.5% of radiation before printing. However, when the printing paste with silver nitrate was present on the sample surface, 99.7–99.9% and 100% of the radiation for 0.01–1% and 10% silver nitrate in a printing paste was absorbed, respectively. Therefore, the energy emitted by the UVC source is regarded as energy absorbed by the samples in this work.

2.4. Reflectance measurements

Reflectance spectra of the cotton textile samples printed with pastes containing silver nitrate were measured with a Spectraflash-light reflectance instrument (Spectraflash 300, D65/10, DataColor, Switzerland). The device was calibrated beforehand, and UV light of 190–400 nm was automatically ceased by software (microMATCH v. 3.6, DataColor, Switzerland), after selecting an option of 0% UV in order not to irradiate the samples unnecessarily. The UV-irradiated samples were measured immediately after irradiation as well as over the next 30 days, to assess stability of the finishing. Typically, reflectance of light (R [%]) was measured for the range of

wavelengths 400–700 nm (10 nm resolution). Then, a wavelength at which the change of the reflectance was maximal was selected and discussed *vs.* absorbed UV energy.

2.5. Washing fastness

After surface finishing, the cotton samples were washed according to a modified PN-EN ISO 105-C06: 2010 (AS1) in order to assess resistance to the washing process. The maximum number of washing cycles was 50. An approximately 3 g weight sample was placed in 150 cm^3 of washing liquor without metal balls, and was washed at 40 °C for 30 min (one cycle) (Scourotester, Hungary). The concentration of the non-ionic active surface agent was equal to 1 g/dm^3 (Rokafenol N8-P7, Boruta Zgierz, Poland). Afterwards, samples were rinsed with water and dried at 40 °C for 40 min (E. Benz, Switzerland). A similar procedure was applied for washing of an A4 size sample prepared according to the description in Section 2.10. In this case, however, the sample was washed in a beaker at 40 °C for 30 min. The washing liquor and the sample were mixed continuously and manually to simulate the washing process. The surfactant and its concentration, as well as rinsing and drying process, were as described above.

Assuming that at a certain absorbed dose of UV light (called the saturation dose) 100% of silver nitrate is converted to a silver product on cotton fabric, it is possible to calculate the relative remained functionality on the cotton fabric after washing following reflectance measurements. The saturation dose is understood to be a dose at which the dependence of the light reflectance for the irradiated printed cotton samples on the absorbed energy of UV light [mJ/cm^2] reaches a plateau (a region of doses of over 2.5 J/cm^2; for the calculations described below, reflectance values at 10 J/cm^2 were taken). The washing fastness indicator (WFI), used also elsewhere (Matyjas-Zgondek et al., 2008), was calculated using the relationship: $WFI = 100\% \times A_{a.w.}/A_{b.w.}$; where $A_{a.w.}$ is the reflectance (500 nm) for the samples after 50 repeated washes; and $A_{b.w.}$ is the reflectance (500 nm) for the samples before washing.

WFI was also calculated after the analysis of samples with ICP-ToF-MS as described in Section 2.6.4. In this case, $WFI = 100\% \times IC_{a.w.}/IC_{b.w.}$; where $IC_{a.w.}$ is signal intensity of ^{107}Ag or ^{109}Ag or the concentration of silver for the samples after 50 repeated washes; and $IC_{b.w.}$ is signal intensity of ^{107}Ag or ^{109}Ag or the concentration of silver for the samples before washing, for semi-quantitative and quantitative variants, respectively (samples UVC irradiated: 10 J/cm^2). The WFI results obtained with all the methods described were compared and are discussed in Section 3.5.4.

2.6. Surface and elemental analyses

2.6.1. SEM and SEM-EDS

A TM-1000 Tabletop Scanning Electron Microscope (Hitachi, Japan) was used for the analysis of the modified cotton. Beforehand, the samples were placed on carbon plasters and sputtered with Au (Cressington Sputter Coater 108 auto, UK). The time of sputtering was chosen experimentally and equaled 12 s. The samples were analyzed at different magnifications, however, the images obtained for the magnifications of 180×, 1000× and 5000× are presented and discussed in this work. Additionally, the samples (modified with 0.01, 0.1, 1.0 and 10% $AgNO_3$ printing paste, irradiated with UVC, 10 J/cm^2, and before and after 50 washes) were measured with SEM-EDS technique: the scanning electron microscopy with field emission S-4700 (Hitachi, Japan) equipped with the energy dispersive X-ray spectrometer (Thermo Noran, USA) for the silver particle distribution studies. Before SEM-EDS measurements the analyzed textile samples were placed on carbon plasters and coated with carbon target using Cressington 208 HR system (Cressington Scientific Instruments Ltd., UK). EDS spectra showing elemental composition were collected from SEM pictures using the same magnification (1000×) for each textile sample. The accelerating voltage for X-ray studies and for SEM images collection was 25 kV, using a probe current of 0.3 nA. The analysis of a sample's diameter and depth for EDS is typically a few micrometers.

2.6.2. ToF-SIMS

Time-of-flight secondary ion mass spectrometer ToF-SIMS IV (ION-TOF GmbH, Germany) was used for identification of elemental and molecular composition of formed silver containing particles (cotton samples modified with 0.01, 0.1, 1.0 and 10% $AgNO_3$ printing paste, irradiated with UVC, 10 J/cm^2, and before and after 50 washes). The ToF-SIMS positive and negative spectra and images (100 μm × 100 μm) were obtained using accelerating voltage set at 25 keV with bismuth primary ion gun (2.5 pA pulse current). A flood gun was used to compensate the surface charging during analysis. In the spectroscopy and imaging modes of TOF-SIMS only the outermost (1–3) atomic layers of the sample were analyzed.

2.6.3. XRD

X-ray diffraction (XRD) patterns were obtained at room temperature using a PANanalytical X'pert PRO MPD diffractometer (The Netherlands), operating at 40 kV and 30 mA (CuK_α radiation). A PANalytical X'Celerator detector based on Real Time Multiple Strip technology, capable of simultaneously measuring the intensities in the 2θ range of 2.122°, was used. All cotton samples, before surface modification and containing a printing paste with silver nitrate, both exposed and not exposed to UVC, as well as before and after washings, were analyzed.

2.6.4. ICP-ToF-MS

The semi-quantitative assessment of the silver content in textile material was performed using inductively coupled plasma mass spectrometer with time-of-flight analyzer (ICP-ToF-MS, OptiMass 8000, GBC, Australia) coupled with the laser ablation system (LA, LSX-500, Cetac, USA). The application of laser ablation system, not requiring any special sample preparation, enables direct analysis of solid materials of trace elements and isotopic ratio even for relatively small amount of sample. On the other hand the main disadvantages are low precision caused by sample inhomogeneity and limitations of quantification (reference materials required). For the optimization process the SRM 612 Glass material (NIST) was used. The analysis was performed for those samples that were modified with printing pastes of 0.01–10.0% (w/w) $AgNO_3$; however, the samples modified with 10% $AgNO_3$ pastes were difficult to measure due to high concentration of silver deposited. Although WFI was calculated for these samples, one should take into account that the results given in Section 3.5.4 may not be precise for such the high concentration of silver nitrate (samples UVC irradiated with 10 J/cm^2; before and after 50 washes). The technique allows for the determination of elemental variation down to trace levels and the analysis of sample's depth of 1–10 μm for a relatively small surface area (10–500 μm).

For the quantitative measurements the textile samples were mineralized in the microwave oven system MILESTONE MLS-1200 MEGA with a concentrated nitric acid (ultrapure; J.T. Baker, USA; 0.2 g of sample/5 cm^3 nitric acid) before the silver concentration determination. The quantitative measurement was performed with inductively coupled plasma mass spectrometer with time-of-flight analyzer (ICP-ToF-MS, OptiMass 8000, GBC, Australia). The ICP-MS technique can be characterized *e.g.* by low detection limits (in general below 10 ppt), wide linear range (up to 10^7), high short-term precision (0.5–2%) and satisfactory stability of the signal with time. The measured amount of silver deposited on cotton samples through printing with 0.01, 0.1, 1 and 10% $AgNO_3$ containing pastes

equaled to 0.000387; 0.003459; 0.025785 and 0.270606 g per 1 g sample, respectively.

2.7. Measurement of waste washing liquor

After washing, the liquor was measured using dynamic laser light scattering (DLS) (Particle Size Analyzer, NICOMP 380, USA). The results of measurements were automatically calculated with the software option of the autocorrelation function analysis *via* application of the NICOMP distribution. This was done in order to assess the distribution of the mean hydrodynamic diameter of the removed particles from the surface-modified cotton. The measurements were performed several times for each waste washing liquor (which was produced for the samples finished with different pastes), both without filtering and after filtration with a 0.45 μm filter (Minisart, Sartorius) to eliminate the cotton dust that was created during washing. The measurements were performed at 23 °C. In addition to the DLS measurements, spectrophotometric analysis of the waste washing liquor was performed. A UV–vis spectrophotometer (Jasco V-530, Japan) was used for this purpose. The absorption spectra were analyzed in the range of 190–700 nm with 1 nm resolution.

2.8. Tensile strength measurements

Tensile strength measurements were performed for warp and weft threads separated from cotton samples, both before and after modification with printing pastes containing silver nitrate and before and after UVC irradiation. Patches of silver-based functionality appeared on the weft and warp of the threads after separation of the threads from the cotton fabric. Only the surface of the threads was covered by the silver-based functionality, and it did not penetrate these inner areas where the treads are tangled. A PC controlled low-load machine for testing mechanical properties of materials (compression and stretching) was used (Zwick 1250, Germany). The instrument was equipped with a measuring 100 N head for stretching and was controlled by the TestXpert software. Three to five threads from each cotton sample were measured in order to examine if any major changes occurred in the structure of threads after modification of cotton, and the averaged results are discussed in Section 3.6.

2.9. Measurements of antimicrobial properties

The antimicrobial properties of the cotton samples were assessed both before and after printing and before and after the repeated washings. Three bacterial strains were chosen: *E. coli* (Gram−: ATTC 11229); *B. subtilis* (Gram+ a strain cultivated at the Lodz University of Technology, Poland, no.: ŁOCK 105); and *S. aureus* (Gram+: ATTC 6538). The agar diffusion test was performed according to the recommendation of the Polish National Reference Centre for Antimicrobial Susceptibility following the American standards published by CLSI/NCCLS (Clinical and Laboratory Standards Institute/National Committee for Clinical Laboratory Standards). In summary, 15 g of broth bouillon was dissolved in 1000 cm^3 deionized water (pH 6.8), and afterwards 15 g of agar was added. The solution was then sterilized *via* autoclaving (15 min). Next, it was cooled to 37 °C and inoculated either with *E. coli*, *B. subtilis* or *S. aureus*. The mixtures were poured on Petri dishes and left for the agar to convert into a physical gel. Afterwards, 20 mm diameter cotton samples were placed on the surface of the gel. Then, the dishes were covered with caps and incubated at 37 °C for 24 h. Subsequently, the inhibition zone for each cotton sample was measured with a slide caliper at different positions around a sample to determine a mean inhibition zone for each sample.

2.10. Example design of antimicrobial protective uniform

An approach to the finishing of cotton in order to obtain antimicrobial workwear is proposed in this study. A cotton textile of the same characteristic as described in Section 2.2 was used. Initially, three stencils were prepared on a woven polyester mesh (EX 63-063/160 PW screen, NBC, Japan; distributed by K+L Company, Poland) stretched over an aluminum frame (screen). Each consisted of part of an apron pattern that was associated with a printing paste containing three concentrations of silver nitrate (0.1; 1 and 10%, w/w). Once the stencils were ready, the cotton textile was printed three times using the stencils.

For the stencil preparation, first a black and white design of two apron parts was prepared in Photoshop CS 8.0 (Adobe Systems Inc., USA). Then, they were printed onto two transparent foils. Next, the photopolymerizable emulsion (Fotocoat 1010–FORTECO, Switzerland) was uniformly distributed on two screens, which were then dried in a drier (SU-6080, Poland) at 40 °C (24 h). After drying, each screen was ready to be exposed to light for creation of a part of the design of the apron immediately on to its surface. For this purpose each foil was placed on one screen and illuminated in a screen exposure system for 3.5 min (Mega-Light, M&R Companies, USA). The light emitted by the lamp passed through the pattern (clear areas) causing polymerization of the photosensitive emulsion. After exposure, the screen was washed in cold water in order to remove the non-polymerized emulsion and was then dried. The areas that were not exposed to light were dissolved, leaving the stencil with the apron part on the mesh, which was a negative of the original pattern. Open areas of mesh transferred a printing paste as a precise image onto a printed cotton fabric. The printing was carried out with the help of a squeegee, forcing the printing paste to move across the stencil toward the threads. Once one part of the apron was printed (with a printing paste containing the first concentration of silver nitrate), the second and the third parts of the apron were printed on the same cotton textile (with a printing paste containing the second and third concentrations of silver nitrate). Afterwards, the printed cotton fabric was removed from under the stencil revealing the printed picture of the apron (white in color) on the cotton textile. Subsequently, the printed fabric was dried at 40 °C for 40 min in order to fix the print based on Helizarin Binder and thus fix the printed pattern. Note that no curing was applied in this case, similar to the printing described in Section 2.2. Finally, the printed fabric was exposed to UVC light of 5 J/cm^2 using the same UV cabinet as described in Section 2.3.

3. Results and discussion

3.1. Development of functionality and stability tests

Cotton fabrics, which were surface-modified with a printing paste containing silver nitrate, change color after UVC irradiation. The development of color is related to the absorbed energy of UV light and the concentration of silver nitrate in the printing paste. This prompted us to assess the samples quantitatively through measurements of light reflectance from the surface of the samples in relation to the absorbed UV energy and concentration of silver nitrate in a printing paste. The results are presented in Fig. 1.

In Fig. 1A, C, E and G, the reflectance spectra are presented for cotton samples that were printed with a printing paste containing 0.01; 0.1; 1 and 10% (w/w) silver nitrate, respectively, and irradiated to the dose of 0–10 J/cm^2. The reflectance spectra change in a wide range of wavelengths. For the lowest concentration of silver nitrate, the spectra change in the range of 400–575 nm, signifying formation of a color product. If the concentration of silver nitrate is increased, the spectra change across the whole examined

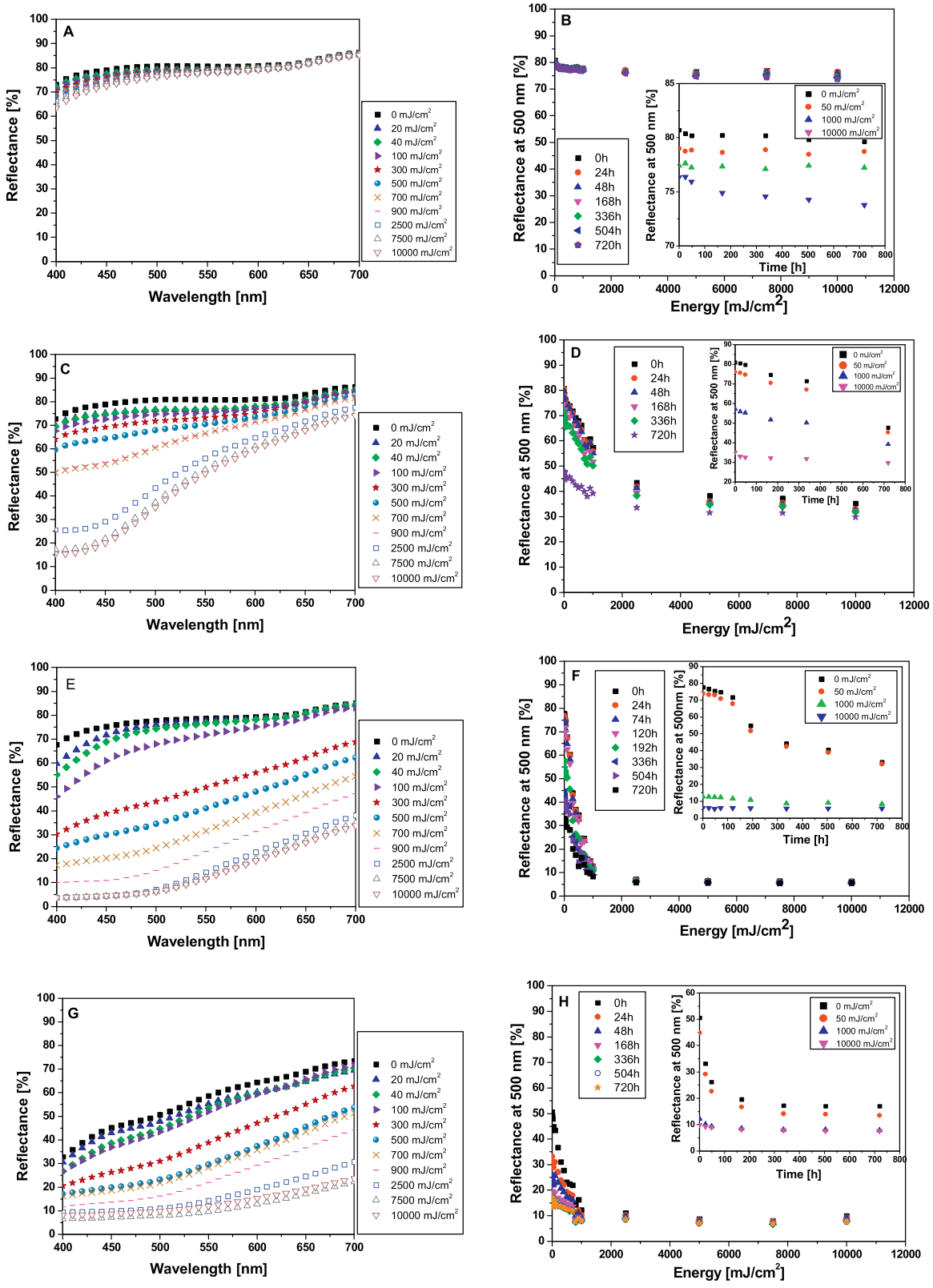


Fig. 1. Elementary characteristics of cotton textile printed with silver nitrate containing a printing paste and irradiated with UV light of 254 nm. Left column (A, C, E, G): reflectance spectra measured immediately after UV irradiation (UV doses are given in the graphs). Right column (B, D, F, H): reflectance (at 500 nm) dependencies on absorbed energy of UV light measured at different times after UV irradiation (the time is given in the graphs); insets: stability of samples during the 30 days (0–720 h) after irradiation was applied at the selected absorbed energies of UV light (UV doses are given in the insets). The results are presented for the samples printed with a paste of the following $AgNO_3$ concentrations: (A and B) 0.01% (w/w); (C and D) 0.1% (w/w); (E and F) 1% (w/w); and (G and H) 10% (w/w) $AgNO_3$.

range of wavelengths. The decrease in the reflectance of light is more pronounced for the samples which were printed with a paste containing higher concentrations of silver nitrate. Moreover, the concentration of silver nitrate in the paste influenced the shape of the spectra, which implies differences in colors of the samples. In fact, it is possible to obtain uniquely colored cotton samples if they were surface-finished with various formulations of the pastes and were irradiated to different doses (see Section 3.4).

The analysis of the reflectance spectra of unirradiated cotton samples revealed that the reflectance tended to be lower across a wide range of wavelengths at higher concentrations of silver nitrate in a printing paste. This is particularly visible for 10% (w/w) silver nitrate in a printing paste, for which the reflectance of light (at 400 nm) is around 50% lower than that for the samples finished with a paste containing 1% (w/w) silver nitrate. A probable reason for this difference is a reduction of silver salt before UVC irradiation and, in consequence, appearance of color. The formation of a silver product for unirradiated samples may be caused by impurities of the fabric, the fabric itself, the paste or occasional short-term exposure of the samples to daylight during transferral after preparation.

In Fig. 1B, D, F and H the long-term stability results for cotton samples printed with a printing paste containing concentrations of silver nitrate of 0.01; 0.1; 1 and 10% (w/w), respectively, and irradiated to doses of 0–10 J/cm^2, are presented. Conversion of silver salt into a silver product is dependent on UV absorbed energy. The samples became saturated at a dose of around 2.5 J/cm^2. The color that appeared on the surface of the samples did not change significantly beyond that dose, which is also discussed in Section 3.4. The lower the concentration of silver nitrate in a printing paste, the higher the stability of the samples. Additionally, if a sample absorbed a relatively high dose of UV light, it was more stable, in contrast to low dose irradiated, or unirradiated, samples. This is easily visible in the insets to Fig. 1, particularly in Fig. 1F and G. The samples that absorbed a dose of 1–10 J/cm^2 were very stable after irradiation and for the next 30 days, whereas those that absorbed 50 mJ/cm^2 stabilized after around 300 h, subsequent to irradiation.

3.2. Washing fastness and stability after washing

The results of the washing fastness are presented in Fig. 2. In Fig. 2A, C, E and G, the light reflectance dependencies on absorbed UV energy are shown for cotton samples printed with a printing paste containing 0.01; 0.1; 1; and 10% (w/w) silver nitrate, respectively, after a different number of washing cycles, measured immediately after irradiation. The distinctive feature of the samples is their resistance to washing. For most concentrations of silver nitrate in a printing paste, we did not observe major changes in reflectance of light between unwashed and 50-times washed samples. In Fig. 2B, D, F and H, long-term stability of silver surface-finished cotton samples was assessed through measuring the reflectance of light after 50 and 1 separate washings (insets in the figures). Samples were stable over a 30-day period. No noteworthy dissimilarity between the samples stored after the washing fastness test was observed over a wide range of absorbed doses for the examined number of washing cycles.

Following the above-described results presented in Fig. 2C, E and G, the functionality level was retained by samples after washing was calculated. WFI was calculated for the samples washed 50 times and equals to: 52%; 64%; 76% for 0.1%; 1; and 10% $AgNO_3$ in a printing paste, respectively. This denotes that most functionality is retained by samples, even after 50 washings. A very low concentration of silver nitrate on cotton fabrics printed with a printing paste containing 0.01% $AgNO_3$, as well as low changes in the measured reflectance of light (Fig. 2A) associated with uncertainty, are the reasons for the difficulty in calculating the percentage functionality remained on samples after washings. WFI assessed through the reflectance of light measurements gives rough estimation of the resistance to washing. This kind of measurement does not take into account the functionality formed in deeper parts of the cotton samples, which are complex in structure, as only surface analysis was performed. Further analysis of WFI is described in Section 3.5.4.

3.3. Measurements of waste washing liquor

The DLS results confirm former observations that washing process removes some silver particles. The measured particles are of polydispersing nature. Fractions of the mean hydrodynamic diameter were seen; however those of up to 5 nm were in the majority in the solutions. Fractions of higher mean diameter may also correspond to the particles of the crosslinking and thickening agents (used in printing paste formulations) combined with silver particles. UV–vis measurements (spectra not shown here) revealed formation of a broad band at 350–550 nm, with the maximum at 435 nm. The absorbance of light in the visible range of wavelengths is related to the light brownish color observed for the waste washing liquors. The intensity of the band is associated with the concentration of silver nitrate in a printing paste that was used for printing of cotton, and so to the content of silver product on the samples. The higher the content of silver on the fabric, the higher is the intensity of the band for waste washing liquors; absorbance at 435 nm ranging from 0.004 to 0.055 for 0.01 to 10% $AgNO_3$ in a printing paste, respectively. Other research also observed a similar spectral range of absorbance for silver nanoparticles solutions (Mahltig et al., 2009; Suber, Sondi, Matijević, & Goia, 2005; Vinci, Bilski, Kotek, & Chignell, 2010; Wei & Qian, 2008). The broad band observed for these washing liquors corresponds to the polydispersity of nanoparticles.

3.4. Colors of cotton-silver samples

When cotton textile samples are printed with silver containing a printing paste and UVC irradiated, the color appears on their surface, depending on the concentration of silver nitrate in the printing paste, the absorbed dose of UV light and the number of washing cycles for the washed samples (Table 1). The samples after printing do not differ from non-printed samples. However, immediately after absorption of less than 50 mJ/cm^2, a color appears. For the range of concentration 0.01–1% (w/w) brown colors dominate, although a contribution of a grayish-color is visible for 1% (w/w) silver nitrate in the printing paste. At higher concentrations of silver nitrate in the printing paste, the cotton samples become gray and dark gray. The strength of color is proportional to the absorbed energy of UV light. The higher the absorbed energy, the more intense is the color. The saturation point, assessed organoleptically, is similar for all samples, and occurs at around 2.5 J/cm^2, which is analogous to that found based on the reflectance of light measurements. Washings cause an increase in the lightness of the samples; however, even after 50 washings, the functionality clearly remains on the samples.

3.5. Surface and elemental analyses

3.5.1. SEM and SEM-EDS

The samples which were UV irradiated to 10 J/cm^2 both before washing and after 50 washings are presented in Fig. 3. The samples that were printed with a printing paste containing either 0.01 or 0.1% (w/w) silver nitrate present similar surface morphology. For this reason, SEM images are not presented here for the samples printed with 0.01% silver nitrate in a printing paste. For these samples, however, we observed that neither the number of the washing cycles nor the dose of UV light significantly changes the surface of the samples. At a magnification of 1000×, we discerned a film

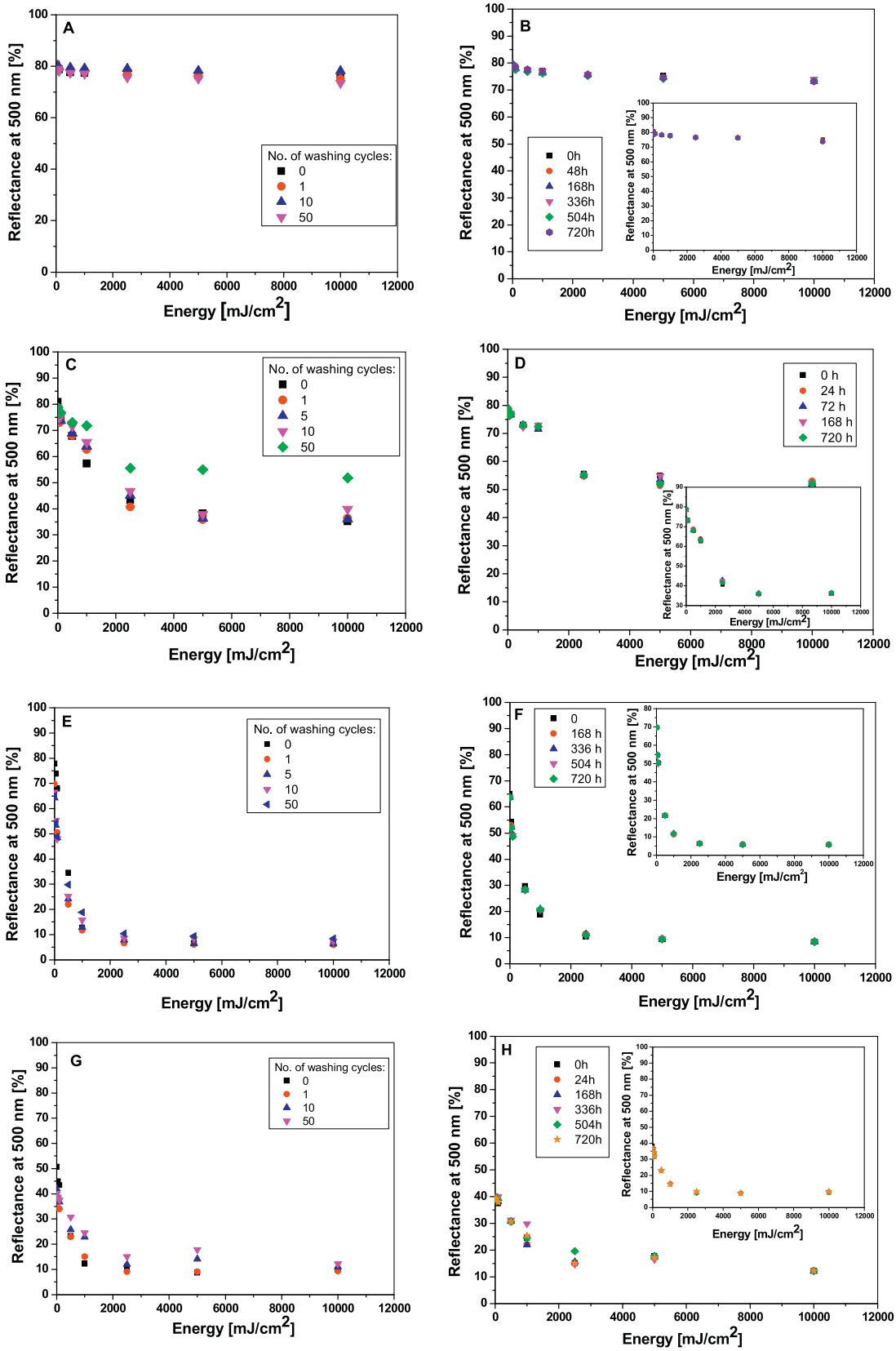
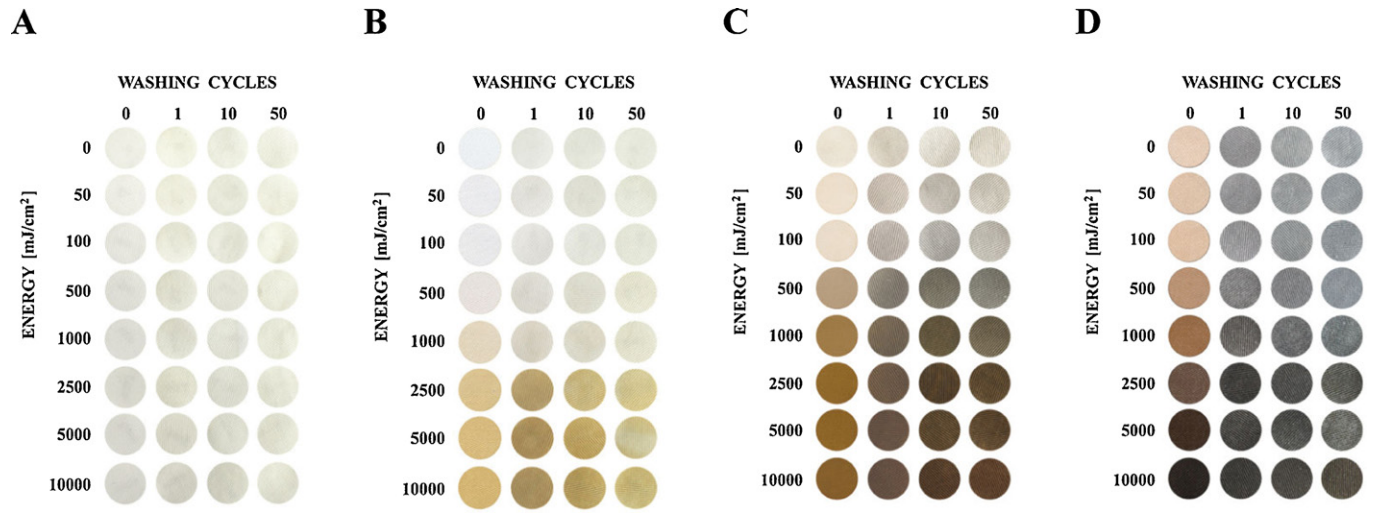


Fig. 2. Left column: washing fastness expressed as reflectance (at 500 nm) *versus* absorbed energy for UV-irradiated cotton textiles printed with printing paste, containing silver nitrate, of the following concentrations: (A and B) 0.01% (w/w); (C and D) 0.1% (w/w); (E and F) 1% (w/w); and (G and H) 10% (w/w) $AgNO_3$. The number of washing cycles is given in the graphs. The samples were measured immediately after irradiation. Right column: stability of washed samples measured during 30 days (0–720 h) after irradiation for 50 washing cycles; and inset: for 1 washing cycle. The results are presented for the samples that were printed with a printing paste containing the following concentrations of silver nitrate: (B) 0.01% (w/w); (D) 0.1% (w/w); (F) 1% (w/w); and (H) 10% (w/w) $AgNO_3$.

Table 1
Analysis of color of cotton samples printed with a printing paste containing 1% (w/w) $AgNO_3$ (CIE Lab color space). The photographs of cotton samples printed with silver nitrate containing a printing paste of different concentrations: (A) 0.01% (w/w); (B) 0.1% (w/w); (C) 1% (w/w); (D) 10% (w/w). The number of washing cycles as well as the UV energy absorbed by the samples is given.

No. of washes	CIE Lab	UVC energy [J/cm^2]							
		0	0.05	0.1	0.5	1	2.5	5	10
0	L	91.02	89.72	87.74	70.44	53.29	45.69	44.06	42.22
	a^*	−0.18	−0.62	0.25	5.97	12.45	15.84	16.12	16.16
	b^*	2.70	6.77	9.66	15.09	29.51	34.39	32.68	28.57
1	L	87.98	79.22	76.09	55.00	45.80	40.53	40.21	40.21
	a^*	1.64	2.74	2.81	3.05	5.27	9.99	12.21	12.21
	b^*	5.10	3.89	3.10	6.92	18.25	25.35	25.93	25.93
10	L	86.10	78.96	73.64	57.86	51.41	46.01	44.96	44.81
	a^*	1.86	2.49	2.00	1.39	3.34	9.87	9.09	12.54
	b^*	4.15	3.34	0.33	6.29	20.29	30.76	29.57	30.87
50	L	85.67	79.32	75.17	61.96	54.54	47.58	47.77	48.39
	a^*	1.52	1.74	1.20	0.61	2.77	6.92	9.82	14.68
	b^*	5.63	4.81	2.19	3.54	14.04	27.86	31.12	32.96



between single threads, formed after deposition of a printing paste. At higher magnifications, a coarse pattern of the film appeared that is a result of screen printing and transferral of the paste through the mesh of a stencil. Single silver product particles and aggregates attached to the fibers could be distinguished sporadically.

The surface of the cotton samples printed with a printing paste containing 0.1% (w/w) silver nitrate was very similar to that described above (Fig. 3). However, we observed a higher number of white spots corresponding to the silver product particles and aggregates. Additionally, the surface of the threads seems to be uniformly covered with a printing paste. At this concentration there appeared as a unique tendency for the samples after washing. Namely, at higher number of washing cycles, the particles and aggregates emerge from the film of printing paste. One can discern brighter spots on the surface of threads after 50 washings, in contrast to the fabric before or after a single washing. This tendency is even more pronounced for the cotton samples printed with a printing paste containing 1% (w/w) silver nitrate (Fig. 3). Additionally, it is very characteristic for this concentration of silver nitrate that the particles are quite uniformly distributed on the threads. They seem to be very similar in size, roughly around 380 nm; however, the particles of 100–1000 nm could be seen as well. The cubic shape of the particles could be discerned.

Higher concentrations of silver nitrate visibly change the rheological properties of the printing paste. Printing of cotton samples with the printing paste resulted in less uniform distribution of the paste on the surface of cotton in contrast to the pastes containing a lower amount of $AgNO_3$ (Fig. 3). One can also see larger patches of the paste with particles embedded between threads of the fabric. Some particles, however, are also attached immediately on the threads. At larger magnification, spherical aggregates of approximately 10 μm diameter can be seen. These may correspond to aggregation of the components of a printing paste: the thickening agent and crosslinker. Similar to the above-described samples, silver product particles emerge from the sample surface after a higher number of washing cycles (Fig. 3). Despite the number of washing cycles, the particles remain on cotton, which is particularly visible for the samples printed with a printing paste containing higher than 0.01% $AgNO_3$.

The surface analysis techniques of SEM-EDS and ToF-SIMS (discussed in Section 3.5.2) are commonly used as complementary tools to the wet chemical analysis enabling the measurement of some volume of a sample (*e.g.* ICP-MS, discussed in Section 3.5.4). SEM-EDS technique can deliver information about the elemental composition on submicrometer level, while ToF-SIMS technique is used on the uppermost monolayers (1–3) level of the studied material and gives the molecular and elemental information. SEM-EDS micrographs of textile samples before and after 50 washes confirmed the presence of silver agglomerates for the samples modified with 10% $AgNO_3$ printing paste. There was a correlation observed between the concentration of silver nitrate in a printing paste and the number of silver-rich particles on the studied material surfaces, which is in agreement with the above-presented results for the SEM analysis without EDS unit. For the samples

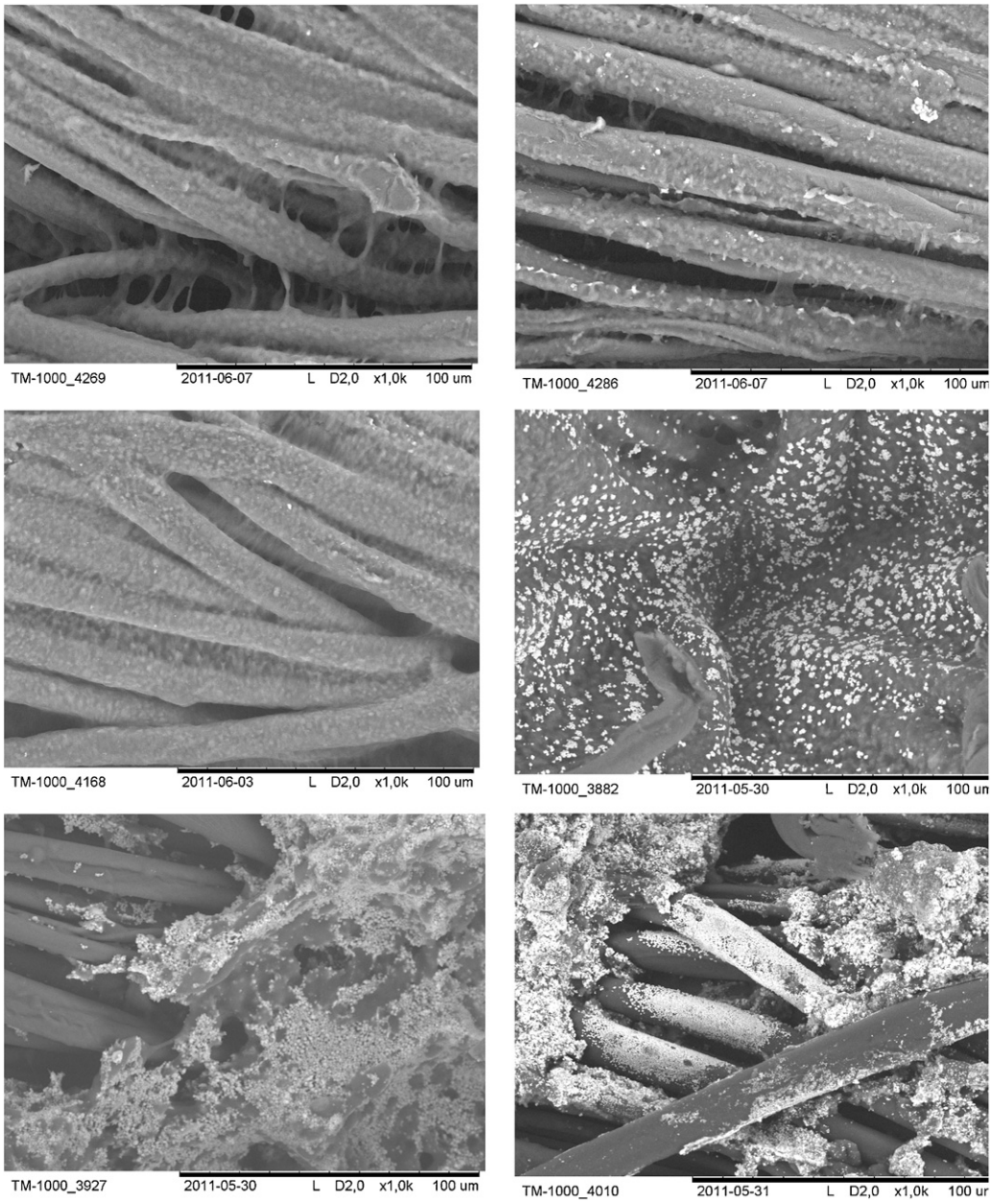


Fig. 3. Scanning electron microscopy of UV irradiated (10 J/cm^2) cotton textile printed with a printing paste containing silver nitrate. Magnification: 1000×; concentration of $AgNO_3$ in a printing paste: first line – 0.1% (w/w); second line – 1% (w/w); and third line – 10% (w/w); left column: before washing, right column: after 50 washings.

containing lower amount of silver, that is those printed with printing paste of 0.01–0.1% $AgNO_3$, the silver containing particles were irregularly distributed on the textile sample surface. It could be observed that the washing process reduced the number of particles rich in silver. For the printing paste of higher silver nitrate concentration (10%), the fibers were almost completely covered by layers of silver agglomerates. Even though the samples were 50 times washed, silver particles were clearly identified, especially for the samples printed with the printing paste containing 10% silver nitrate.

Silver on the samples printed with 0.01–0.1% $AgNO_3$ printing pastes was not identified on the EDS spectra, which were collected from the samples surfaces. This is due to a potential detection limit of SEM-EDS technique that is about 0.1–0.5% (w/w) for most elements. However, it was identified on those samples that were printed with printing pastes containing 1–10% $AgNO_3$ before and even after 50 washes. The sulfur was not present on the obtained spectra which may suggest that the formation of silver sulfides is quite questionable. After 50 washes of those samples printed with 10% $AgNO_3$ containing paste, peaks of Al, Zn, Cl, K and Ca were observed apart from the peaks of silver. For the same samples not submitted to the washing process the following elements were detected: Na, Al and Si, which may indicate that the contaminants of Zn, Cl, K and Ca are introduced into the samples during the washing. No correlation could be observed between the printing paste used and silver peaks intensities, which might be a consequence of the silver aggregates formation on threads. These results obtained imply that the most likely silver products formed on cotton fibers are those in the oxide form.

3.5.2. ToF-SIMS

Using the ToF-SIMS technique the presence of secondary ions of silver and its compounds with oxygen and chlorine on the surface of the textile samples was confirmed. In the secondary ions mass

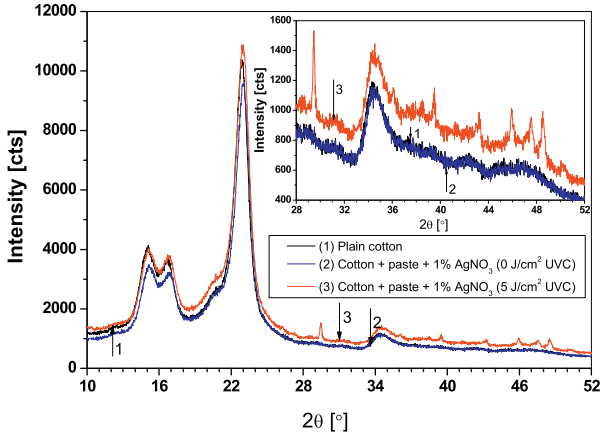


Fig. 4. X-ray diffraction patterns of cotton textile before surface modification (1); after printing with a printing paste containing 1% $AgNO_3$ (2); and after printing with a printing paste containing 1% $AgNO_3$ and exposed to UVC (5 J/cm^2) (3). Inset: different range to visualize difference between (3) and (1) and (2).

spectra (positive mode) the peaks of silver, silver chloride and silver oxide were detected. The ToF-SIMS images (500 μm × 500 μm) showed that the distribution of AgCl ions on the sample's surface is quite homogenous. No presence of silver sulfides was observed. Using this technique we could not definitely conclude about the possible form in which silver exists on the surface of such the complex samples.

3.5.3. XRD

XRD diffraction studies showed (Fig. 4) that the plain cotton used in this study had an amorphous structure and gave diffuse rings at $2\theta = 14.9°$; 22.8°; and 34.5°. The cotton containing silver nitrate and a printing paste produced the same rings as the plain cotton, arguably due to fine dispersion of silver nitrate in the fabric. Only after absorption of UVC energy by cotton fabric after printing with paste containing silver nitrate did the different rings appear, implying some crystal structure formation on threads. Such samples had an amorphous structure, with the diffuse rings in the same region as in the case of the plain cotton. In addition, some new peaks appeared at $2\theta = 29.1°$; 39.1°; 42.9°; 47.3°; and 48.2°, which indicated the presence of silver ions on the cotton, possibly attributable to incomplete reduction of silver nitrate. However, no clear indication was found as to the product formed on cotton. For instance, the rings could not be firmly attributed to either silver nanoparticles (zero valence state) or silver oxides. Additionally, no difference in X-ray diffraction was observed for the samples containing the applied range of silver nitrate concentrations that were irradiated at different dose levels, as well as for those that were before or after washing.

On the whole, the results obtained with the aid of the applied analytical techniques: XRD and ToF-SIMS, suggest that the determination of exact composition of the silver product formed is difficult. However, the silver product formed on the samples may be oxidized or may exist in the form of chlorides; most likely silver sulfides are not present in the samples.

3.5.4. ICP-ToF-MS

Semi-quantitative analysis revealed that the percent of silver removal after the washing process was the highest for the lowest concentration of silver in the printing paste used and decreased with the increase of silver amount in the paste applied for surface modification of cotton samples. The correlation between the intensity of signal for both silver isotopes and the silver concentration was observed. The intensity of peaks increases about 10 times with the increase of silver concentration in the pastes. WFI for the silver modified cotton samples assessed with the semi-quantitative variant of ICP-ToF-MS was found very similar for ^{107}Ag and ^{109}Ag and equaled 42.3 and 42.5%; 35.7 and 37.5%; 87.9 and 85.9%; and 80.1 and 80.2% for these isotopes and for 0.01, 0.1, 1 and 10% $AgNO_3$ in the printing pastes used for the samples' surface modification, respectively. It is believed that the WFI for 0.1% $AgNO_3$ printing paste may be associated with an experimental error stemming from inhomogeneous finishing of the sample's surface. Nevertheless, these results correspond to the WFI calculated with the aid of the light reflectance measurements. Similar tendency was observed. The samples modified with the printing pastes of the higher silver concentration characterized with higher WFI. Much lower values of WFI were obtained in the case of quantitative variant of ICP-ToF-MS; WFI equaled: 10.6, 26.3, 24.6, 28.3% for the samples printed with 0.01, 0.1, 1 and 10% $AgNO_3$ printing pastes, respectively, however, the tendency mentioned above is the same in this case as well. The difference in WFI values may be associated with the measurement methods applied. WFI calculations based on the measurements of the reflectance of light and silver content through the semi-quantitative ICP-ToF-MS took into account only the very surface of the samples. Consequently, the results are quite similar. However, in the case of the quantitative ICP-ToF-MS the whole samples were analyzed since they were mineralized. Therefore, it may be concluded that the functionality formed on the surface of the samples is resistant to 50 washings, whereas untransformed silver from the printing paste in the deeper parts of the samples is lost during the washing process, which in consequence lower the WFI in the case of the quantitative analysis.

3.6. Tensile strength of the samples

Measurements of the tensile strength of samples revealed substantial differences in warp and weft threads. In all examined cases, warp threads were characterized by a higher maximal stress and lower maximal strain, in comparison to weft threads. Consequently, the Young modulus was higher for warp threads. For instance, the Young modulus [MPa], maximal strain [%] and maximal stress [MPa] for plain cotton equaled 21.2; 3.7; and 254.2 for warp; and 1.5; 8.6; and 110.2 for weft, respectively. The difference between warp and weft threads is associated with the characteristics of the threads; that is, the warp threads had a 50% smaller diameter (0.134 mm) than weft threads. The results for warp and weft threads determined from the different samples were compared. For instance, maximal strain and Young modulus for warp threads of the samples printed with a printing paste containing 0.1 and 10% $AgNO_3$ and UVC irradiated (5 J/cm^2) equaled 5.2 ± 1.1; 14.0 ± 4.3 and 4.3 ± 0.5; 18.7 ± 8.7, respectively. However for the weft threads, the maximal strain and Young modulus equaled 6.7 ± 0.5; 3.7 ± 1.1 and 7.9 ± 1.3; 2.4 ± 1.1, respectively. Therefore we concluded that no major difference was observed for the samples modified with printing paste containing silver nitrate and UVC-irradiated, independent of the absorbed dose. Consequently, the functional finishing method does not reduce the mechanical properties of samples.

3.7. Microbiological studies

After measurements of the *E. coli*, *B. subtilis* and *S. aureus* proliferation inhibition zones, corresponding graphs were drawn (Fig. 5) to illustrate the correlation between the zones and the concentration of silver nitrate in a printing paste, the amount of UV light energy absorbed by the samples, and the number of washing cycles. The microbiological analysis revealed that all samples inhibit proliferation of the bacteria both before and after 10 washings, and almost all samples inhibit proliferation after 50 washings. Only

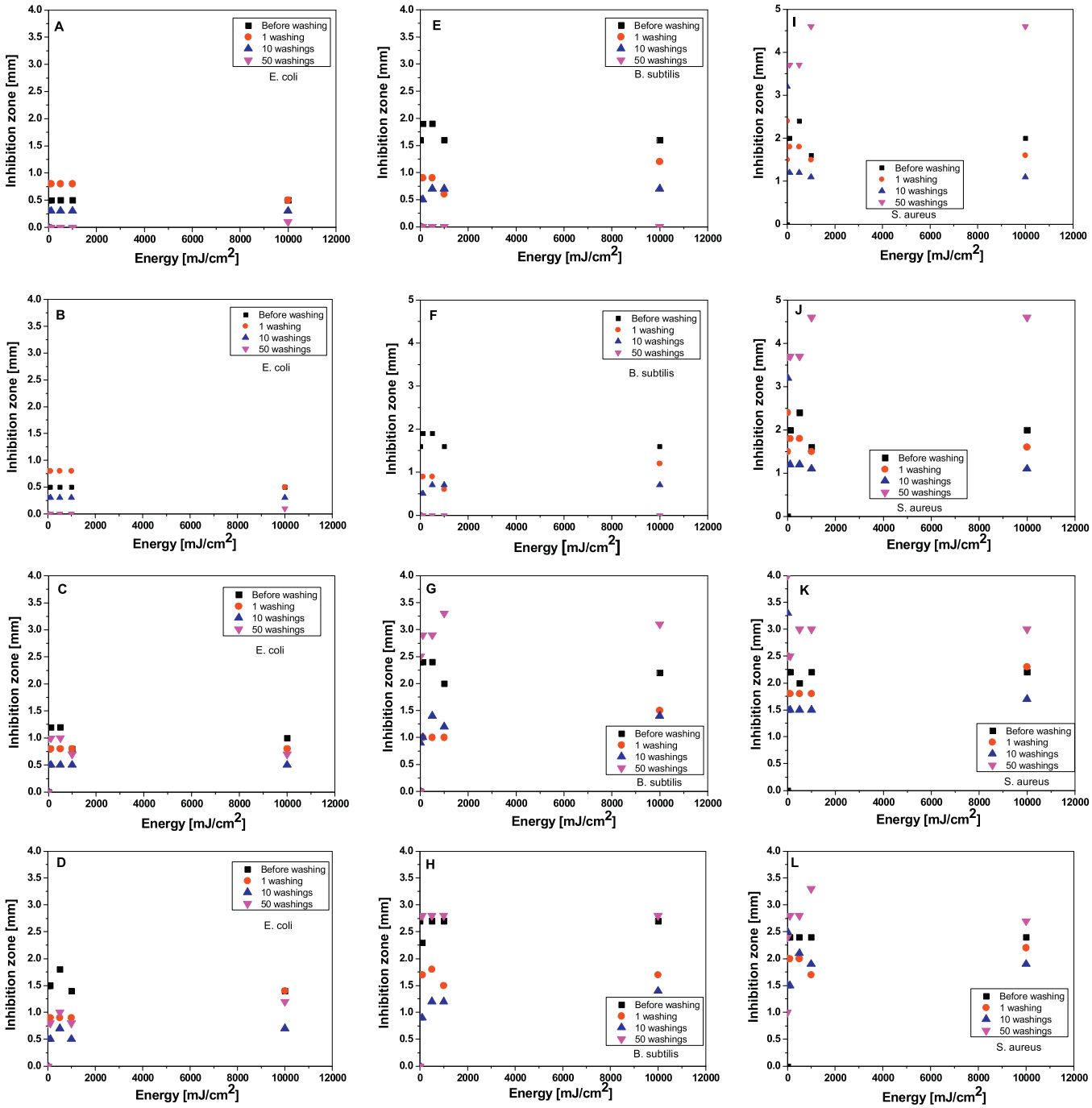


Fig. 5. Inhibition zones obtained from agar diffusion tests for cotton textile printed with printing pastes containing different concentrations of silver nitrate, from upper to lower graph in columns: 0.01%; 0.1%; 1%; and 10% (w/w) $AgNO_3$. The results are presented for: *E. coli*, (A)–(D); *B. subtilis*, (E)–(H) and *S. aureus*, (I)–(L).

the samples that were printed with a printing paste containing 0.01–0.1% (w/w) silver nitrate and washed 50 times provided no protection against *E. coli* and *B. subtilis* (Fig. 5A, B, E and F). The lowest inhibition zones were observed for *E. coli.* The inhibition zone was not seen to be dependent on the dose of UV light absorbed by the samples. However, the magnitude of the inhibition zone is related to the concentration of silver nitrate in a printing paste. Generally, the higher the concentration, the larger is the inhibition zone of the samples. We also observed untypical behavior of the samples after multiple washings, which is at variance with the usually expected results described elsewhere. Namely, in some cases the inhibition zones increased after 50 washings to a larger extent than those for the unwashed samples, for instance: for *B. subtilis*, concentration of $AgNO_3$ in a printing paste, 1 and 10% (w/w) (Fig. 5G–H); and for *S. aureus*, concentration of $AgNO_3$ in a printing paste, 0.01–10% (w/w) (Fig. 5I–L). This can be explained when taking into account the results obtained from the surface analysis of the samples with the aid of scanning electron microscopy. In fact, we observed that washing removed some silver particles, therefore causing an increase in the lightness of the samples, but could also facilitate uncovering silver particles from the polymeric film formed on the threads. Therefore, during the repeated washings, silver particles and aggregates emerge from the surface of the cotton textile. As a consequence, the samples showed higher activity against the strains of bacteria.

Fig. 6. Photographs of example protective uniform: (A) a cotton cloth after printing; (B) the same cloth after UVC irradiation (absorbed dose equaled to 5 J/cm^2); and (C) after one washing. (For interpretation of the references to color in text, the reader is referred to the web version of the article.)

3.8. Example design of antimicrobial protective uniform

Cotton fabric was printed to demonstrate a likely application of the results for the elementary characterization of UV-assisted antimicrobial finishing of textiles. A pattern was chosen to mimic an apron, as an item of protective workwear. Areas of the pattern were printed with printing pastes containing different concentrations of silver nitrate, but also irradiated by the same dose of UV. The results are shown in Fig. 6 for the sample before and after UV irradiation, as well as after UV irradiation and washing. One can easily discern development of functionality caused by absorption of UV energy (Fig. 6B). The colors of the various parts of the apron are related to the concentration of silver nitrate in the printing pastes, which was also shown for plain samples in Table 1. Note that the beige color of the middle part of the apron corresponds to the self-transformation of silver cations into a silver product at high concentration of silver nitrate in a printing paste (10%). Washing of the sample caused some changes in colors of some parts of the apron. The colors of the different parts of the apron are associated with different properties for inhibiting bacterial proliferation, as shown above. Therefore, one can design a workwear garment so that different parts inhibit bacterial proliferation according to need. The proposed method for functionalization of textiles also possesses a creative design aspect.

4. Conclusions

This work presents a method by which cotton fabric can be finished antimicrobially through *in situ* preparation of silver functionality on threads by means of screen-printing with printing paste containing silver nitrate and exposure to UVC light. An immediate effect of the irradiation is development of color. The color and its strength are related to the absorbed dose of UV light and the formula of a printing paste. It may also change after washing. Those cotton samples that were irradiated above the saturation dose (assessed to be around 2.5 J/cm^2) were shown to be stable over longer periods of time. No changes in mechanical properties were observed for the modified cotton.

Washing fastness tests revealed that some functionality is removed from the samples after each wash, although generally they are resistant to 50 washings. The washing fastness indicator calculated for the samples depends on the adopted method of the samples measurements. The semi-quantitative ICP-ToF-MS and the reflectance of light measurements gave similar results indicating high resistance to washing of the functionality formed on the samples' surface, whereas quantitative ICP-ToF-MS showed that much silver nitrate is in deeper parts of the samples, which was probably unconverted after UVC irradiation, is removed during the washings.

A distinctive feature of the silver-finished cotton samples is their antimicrobial activity toward *E. coli*, *B. subtilis* and *S. aureus*. Moreover, a higher number of washings is one explanation for increased antimicrobial action of the samples which, according to our knowledge, is not reported for similar studies. Scanning electron microscopy with energy dispersive X-ray spectrometry revealed that silver nanoparticles were formed, and that washing encourages the nanoparticles to emerge from printing pastes. This affects the antimicrobial action of the samples. In spite of XRD, SEM-EDS and ToF-SIMS analyses performed, no clear experimental indication on the chemical form of the silver product can be given.

The proposed method of cotton functionalization also has an artistic design aspect. It is possible to create a range of colors on cotton through variation of the printing paste formula, absorbed dose of UV light, and number of washings. It should be emphasized that the method is not limited to printing on cotton.

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